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Preface

Tracer advances in catchment hydrology

INTRODUCTION

Tracers have become common to hydrological investigations because they specifically offer information about the age, origin and pathways of water and serve as useful tools for evaluating conceptual or numerical models. Tracers, whether artificial (deliberately added to the environment) or environmental (introduced by natural processes), have led to new insights in catchment hydrology such as the role of 'pre-event' water in stormflow response, ages of water in catchments or identifying water sources supporting run-off generation or plant–water uptake.

We now know that comprehensive understanding of hydrological processes in catchments is not possible based on physical characterization alone. While observations of hydraulic heads, flow rates and physical properties of catchments are useful in establishing internal state properties and boundary conditions, they provide an incomplete picture when it comes to understanding the age, origin and pathways of water in catchments. That is because many of our measurements characterize the celerity of hydraulic potentials rather than the velocity of the water itself, which can be orders of magnitude slower (McDonnell and Beven, 2014). Tracers offer a tool to characterize water velocities and pathways even in complex, heterogeneous subsurface environments.

Over the last several years, there has been a flood of review papers and commentaries tackling topics related to tracers in catchment hydrology. Topics have included the use of tracers to assess flow paths, storage and run-off generation (Tetzlaff *et al*., 2015a), water transit time (McDonnell and Beven, 2014; McDonnell *et al*., 2010; Rinaldo *et al*., 2015; Soulsby *et al*., 2009; Stewart *et al*., 2012), hydrograph separation (Klaus and McDonnell, 2013) and ecohydrological separation (McDonnell, 2014). The community has moved from the use of tracers in simple models that describe the separation of streamflow into 'event' and 'pre-event' water components (e.g. Sklash *et al*., 1976) to more complex models that describe dynamically the age spectrum of streamflow (e.g. Harman, 2015). Separation of water sources has advanced from hydrograph separation to ecohydrological separation where now we are developing a better understanding of the role soils play in partitioning water between vegetation and drainage (i.e. streamflow generation or groundwater recharge) (Evaristo *et al*., 2015). Unlike the rather bleak assessment of isotope-based hydrograph separation by Burns (2002), tracer techniques have flourished of late and moved to the forefront of tools that are yielding new insights into catchment processes.

This special issue on tracer advances both reviews this evolution of using tracers in catchment hydrology and provides examples of new cutting-edge techniques, which inform the future outlook of tracers in catchment hydrology. The emphasis on tracer application to catchment scale problems was the main criteria for selecting papers. Papers were solicited to cover a range of processes in catchment hydrology from soil water storage to run-off generation to evapotranspiration with a focus on water stable isotopes and conservative solutes. However, recognizing that other tracers are being used and there are numerous emerging tracer techniques in catchment hydrology (e.g. Bullen, 2014; Haggerty *et al*., 2008; Sharma *et al*., 2012), we included examples of such new tracers that are being used in run-off generation studies. Tracers and applications typically used in groundwater investigations were not included in this special issue, but have been recently reviewed elsewhere (e.g. Sanford *et al*., 2011; Turnadge and Smerdon, 2014).

Several themes emerge from the collection of papers presented in this special issue: (1) ecohydrological separation and water partitioning in the soil water domain, (2) integrating hydrological models with tracers to improve understanding of catchment function and (3) new tracers and tracer applications in new catchment environments. Together, these three themes illustrate major research areas in catchment hydrology. Theme 1 deals with critical questions related to the soil–plant–atmosphere continuum at the scale of a catchment. In other words, the papers in this theme are aimed at understanding how soil water contributes to evaporative processes or run-off processes based on the nature of water stable isotopic variation between pools of water in the catchment. It is interesting to note that Kennedy *et al*. (1986) raised this as an issue almost 30 years ago. Recent work has hypothesized that low and high mobility soil water do not readily mix, and this causes differences between water that becomes transpiration and water that participates in recharge or run-off generation (e.g. Brooks *et al*., 2010). Papers in Theme 1 address some of the emerging areas in this study of ecohydrological separation. Theme 2, which focuses on improving hydrological modelling and our conceptualizations of how water is transported and stored in catchments, is also a dominant research area in hydrology. Several of the papers presented in this issue describe how using tracers in rainfall–runoff models lead to a more generalized modelling framework, where not only water fluxes are resolved, but transport is explicitly included. Indeed, this is a grand challenge in catchment modelling where being right for the right reasons (Kirchner, 2006) means getting both the celerity (i.e. speed with which a perturbation to the flow, such as pressure, propagates through the flow domain) and the velocity of water correct (McDonnell and Beven, 2014). The three papers in Theme 3 present new tracers and new tracer applications and illustrate how tracer hydrology is continually evolving into new landscapes and with new tools.

Theme 1: ecohydrological separation and water partitioning in the soil water domain

The theme of ecohydrological separation and water partitioning in the soil water domain covers soil water extraction techniques for stable isotope analysis (Geris *et al.*, 2015; Sprenger *et al.*, 2015), evaluating ecohydrological separation and hydrologic partitioning among storage compartments (Geris *et al.*, 2015; Tetzlaff *et al.*, 2015b) and liquid-vapour water exchanges between soil water and the sub-canopy environment (Green *et al.*, 2015). These studies demonstrate the usefulness of water stable isotopes in understanding how water is partitioned between different flow pathways and phases within catchments. However, these papers show that it is critical to accurately characterize the isotopic composition of each water source to make inferences about processes such as plant water uptake from soil. For example, Sprenger *et al.* (2015) and Geris *et al.* (2015) show that depending on which soil water extraction method is used, the isotopic composition can vary creating uncertainty in the identification of water sources that trees are accessing. Likewise, Green *et al.* (2015) proposed two scenarios to explain an increase in deuterium excess (cf. Dansgaard, 1964) that they observed, which they suggest was related to sub-canopy water recycling (i.e. evapotranspiration and then re-condensation). However, they were not able to confirm the underlying mechanisms responsible for their observations partly because of the lack of information on vapor isotopic composition.

Theme 2: integrating hydrological models with tracers to improve understanding of catchment function

The use of tracers in estimating water age has a long history in hydrology going back to the work of Nir (1964) and Dinçer *et al.* (1970). Yet, over the last 15 years, there has been an explosion of papers on water age in catchments. Until recently, most water age studies had assumed that the distribution of ages was time invariant (e.g. McGuire and McDonnell, 2006). Time variant (non-stationary) approaches to modelling the transit time of water began gaining traction about 5 years ago. A series of papers had demonstrated its broad applicability and contributed new theoretical formulations for describing the transport of conservative tracers through catchments, and estimating the time-variant age distribution of water in catchment storage and outflows (Botter *et al.*, 2010; Hrachowitz *et al.*, 2010; Rinaldo *et al.*, 2011; van der Velde *et al.*, 2010). In this issue, Benettin *et al.* (2015) summarize this theory and describe backward and forward time concepts, which are central to understanding fate and transport of solutes and tracers in catchments.

Beven and Davies (2015) expand on transport concepts by simultaneously mapping flow and transport dynamics to explore the nonlinearity of catchment responses and how they evolve in phase space (i.e. storage-discharge, storage-residence time and other storage-response variable relationships). Their particle tracking approach provides new insights into the structure of the flow/transport response that may guide new formulations of hillslope and catchment process representations. This goal is expanded upon by Birkel and Soulsby (2015) in their review of how tracers have been incorporated in rainfall–runoff models, and how the differences between the timescales of the celerity of the rainfall–runoff response and the timescales of the pore velocity of water help constrain or conceptualize process representations in catchments. They evaluate progress in tracer-aided modelling and put forth several research frontiers that are expected to advance our understanding of catchment hydrology. Specifically, one of the areas they point to, i.e. investigating the nonlinear, threshold-type, non-stationary and hysteresis driven nature of how catchments process water and solutes – is the very core of the Beven and Davies (2015) analysis. Hrachowitz *et al.* (2015) take an applied approach to examine these same linkages between celerity and transport (i.e. mass flux) responses and explore whether model formulations that include these processes can reproduce biogeochemical patterns that are observed in a test catchment. They explore the now commonly described near-stationary solute behaviour (Basu *et al.*, 2010; Godsey *et al.*, 2009) and the fractal (1/f) scaling of stream chemistry (Godsey *et al.*, 2010).

Theme 3: new tracers and tracer applications in new catchment environments

New tracers that elucidate flow paths or quantify contributing sources are needed because other tracers such as water stable isotopes are limited in their ability to discriminate geographic or spatially explicit zones in catchments. Geochemistry has historically been used to aid in the determination of water sources (e.g. Burns *et al*., 2001; Genereux *et al*., 1993); however, there are emerging tracers that show strong promise in resolving water sources and flow paths. One example presented in this special issue is the use of synthetic deoxyribonucleic acid (DNA). The potential benefit of DNA tracing is that the number of possible unique tracers is practically limitless, and different DNA should have essentially identical transport properties. Dahlke *et al*. (2015) compared synthetic encapsulated (i.e. biodegradable microspheres) and non-encapsulated DNA tracers with a fluorescent dye tracer in a small valley glacier as a test case to demonstrate the potential in using DNA as a hydrologic tracer. While mass recovery of both types of DNA tracers was low compared with the fluorescent dye tracer, breakthrough curves revealed identical peak arrival times and similar dispersion coefficients, suggesting transport was similar for both tracers. This study suggests promise for multi-tracer applications of direct labelling and tracing of multiple water sources and flow pathways that would yield spatially explicit information regarding catchment run-off processes.

Another example of a novel tracer is the use of diatoms that occupy terrestrial habitats that are also associated with run-off generation areas. Pfister *et al*. (2009) first described the potential of diatoms to trace flow paths in catchments. The paper by Klaus *et al*. (2015) builds on this earlier work and describes the occurrence and classification of drift diatoms (i.e. diatom species that occur in moist terrestrial habitats, such as riparian areas, soils and rock surfaces). They document the diatom dynamics during a run-off event, and show the potential usefulness of diatoms as a tracer of hydrologic connectivity between riparian areas and hillslopes.

Novel tracers and techniques are not necessary to advance our understanding of catchment hydrology. As Jefferson *et al*. (2015) illustrate, a standard isotopic hydrograph application can have profound implications for understanding water sources in systems that are generally not well characterized hydrologically. This is the case for urban headwater catchments where stormwater control structures and other infrastructure bring additional layers of complexity to the rainfall–runoff process. Very few studies have yet examined isotopic tracers in urban watersheds. Jefferson *et al*. (2015) applied two-component isotope mixing models to a series of storm events and were able to show the contribution of run-off over time from stormwater control structures. Their analysis revealed a varying residence time within a stormwater control structure, which ranged from a few hours during high flows to days or weeks as water from one event was mixed with water from previous events.

Summary

This special issue clearly highlights the contribution of tracer studies to catchment hydrology. It is fair to say that no other hydrological tool has contributed more to the understanding of the age, origin and pathway of water movement in catchments than tracers. The advent of new technologies has reduced costs and effort required to obtain tracer data such as stable isotopes (Keim *et al*., 2014), and modelling tools are becoming increasingly accessible (CUAHSI, 2015).

We expect additional advances coming from tracer applications as researchers continue to grapple with questions related to water sources, the timing of water movement and storage, and pathways by which water travels within catchments. These questions are fundamental to catchment hydrology and the contribution of hydrology to the understanding of critical zone, climate change and ecosystem science.

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